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CMI REPORT ON PROJECT 2.3.2 ACTIVITIES: 09/2013 TO 03/2014

P. E. A. Turchi, P. Soderlind, A. I. Landa, V. Lordi

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2. DEVELOPING SUBSTITUTES (A. SCHWARTZ, LLNL; B. SALES, ORNL)

2.3 THRUST 3: MATERIALS DEVELOPMENT FRAMEWORK (V. Bulatov, LLNL; D. Singh, ORNL; D. Johnson, Ames)

2.3.2 Project 2. Materials Design Simulator – Efficient Prototyping of Rare Earth-Based Alloys from *ab initio* Electronic Structure and Thermodynamics (Lead: P. Turchi, LLNL; with P. Soderlind, A. Landa, V. Lordi, LLNL; D. Johnson, Ames Lab; K. Rajan, ISU)

Content

I. Project Description

1) Objective: The objective of this project is to develop and apply a Materials-Design Simulator (MDS) for predicting thermodynamic phase stability, structural and magnetic properties, and performance of complex REE-based materials. We seek to create a knowledge base for identifying alloys with desirable properties.
2) The aim of this project is to develop an efficient infrastructure for creating a knowledge base for identifying new alloys with enhance performance and reduced REE-content, and for managing material data acquired within the Focus Area 2 and with input from Focus Area 4.
3) Technology: This project integrates two approaches to alloy process modeling that so far have been developed largely independently: (1) electronic structure theory of alloys and (2) semi-empirical methods of computational thermodynamics and kinetics (such as CALPHAD). This project will greatly benefit from experimental data on phase characterization, heat of formation (from differential scanning calorimetry), and magnetism as a function of pressure to support the search for REE substitutes without compromising on target properties for applications. The MDS will be also greatly enhanced through the use of state-of-the-art methods of materials informatics and data mining.

4) Potential use: The MDS will facilitate examination of research results, discovery of trends, identification of knowledge gaps, and even possibly underlying scientific principles, MDS will be developed and assembled for gathering, accessing, and analyzing available material data generated externally and within CMI projects by experimentalists and modelers. The data in our knowledge base will be accessible to all hub participants via a web interface and underlying engine that will allow targeted searches through heterogeneous data on composition, property and structure spaces encompassing all contributed data.
5) The project essentially funds CMI members. In FY14, fees for software (thermodynamic Thermo-Calc) maintenance and updates will have to be included in the budget.
6) Work is essentially performed at LLNL in collaboration with Ames (D. Johnson), and Iowa State University (Krishna Rajan).
7) By combining input energetics from electronic structure theory of alloys with semi-empirical methods of computational thermodynamics and kinetics within the CALPHAD (CALculation of PHAse Diagrams) framework, the prediction of optimum structures and alloy magnetic properties in REE-based alloys that minimized the usage of REE will be accomplished with our MDS that will relies on a search engine based on the Mesh Adaptive Direct Search (MADS) algorithm. The MDS elements are summarized in Figure 1.

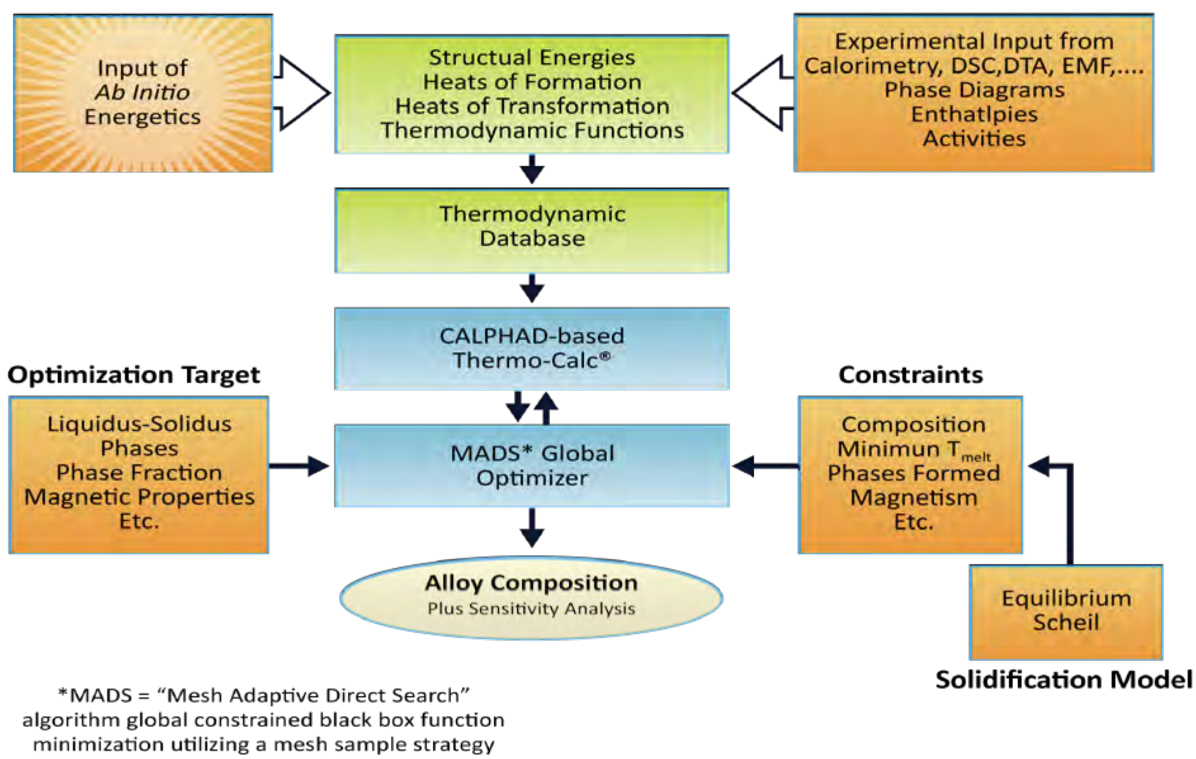


Figure 1. Schematics of the materials-design simulator (MDS) for optimizing materials properties.

8) Impact on Science and Technology: The MDS will have the advantage of coupling the best available experimental data and the advanced modeling tools for predicting thermodynamics, structure-properties relationships, and performance of complex RE-based materials under normal and unusual external conditions of temperature, and pressure, and therefore their thermal and mechanical integrity. Ultimately the modeling package will provide critical guidance for the experimental design of new RE alloys and compounds, and

suggestions for experiments that uniquely certify the accuracy of the simulator, and guarantee the accelerated and safe insertion of materials into application. At the same time, experimental probing of materials properties will provide a crucial insight to improve modeling assessment and prediction of materials properties.

II. Relation of Project 2.3.2 to other Projects (as of March 2014):

Based on discussions that occurred during several conference calls and at LLNL with other teams in Focus Areas 2 and 4, the relations of our project 2.3.2 to the following projects has been identified:

III.2.1.1 Project 1. Reduced Rare Earth Content High Performance Magnets (Lead: S. Bud'ko, Ames; with Canfield, Johnson, Ames; Parker, Sales, Singh, ORNL)

III.2.1.2 Project 2. Additive Manufacturing of Permanent Magnets (Lead: S. McCall, LLNL; with Kuntz, Moore, LLNL; Sun, Brown; Paranthaman, Dehoff, McGuire, Miller, ORNL; McCallum, Kramer, Ames; Trout, Molycorp)

III.4.1.1 Project 1. Ab initio Theory of Temperature Dependent and Multi-Scale Phenomena in Magnets (Lead: V. Antropov, Ames; with Sadigh, LLNL)

III.4.1.3 Project 3. Fundamental Properties and Phase Diagrams (Lead: R. Riman, Rutgers; with Moyer, ORNL; Navrotsky, UC-D; Anderko, OLI; Zhou, Ames)

III.4.1.4 Project 4. Rapid Assessment Methodologies (Lead: R.W. McCallum, Ames; with Kramer, Ott, Pecharsky, Gschneidner, Ames; Riman, Rutgers; Navrotsky, UC-D)

III. Research Team and Level of Effort

The undertaking of this project is particularly compelling at this time since the coupling between *ab initio* results and the CALPHAD approach has successfully been implemented at LLNL allowing prediction of thermodynamic-related properties of complex multi-component *f*-electron alloys relevant for the development of high burn-up advanced nuclear metallic fuels for next generation nuclear reactors.

The LLNL team consists of senior scientists, Drs. Patrice E. A. Turchi, Per Söderlind, Alex Landa, and Vincenzo Lordi who are known for their leading role in the development of advanced theoretical tools and their applications to the prediction of the properties of complex alloys. The team has particular experience with electronic-structure calculations for *f*-electron systems with close to 100 publications on the subject. These scientists will apply theoretical tools to provide new physics-based knowledge on alloyed REE-based compounds and alloys and guide the selection of benchmarked experiments.

Name	Institution	E-mail	Phone #	Effort (FTE) June to Oct.	Effort (FTE) Nov. to Present
Patrice E. A. Turchi	LLNL	turchi1@llnl.gov	(925) 422-9925	0.30	0.20
Per A. Söderlind	LLNL	soderlind1@llnl.gov	(925) 423-4667	0.30	0.20
Alexander I. Landa	LLNL	landa1@llnl.gov	(925) 424-3523	0.30	0.20
Vincenzo Lordi	LLNL	vlordi@llnl.gov	(925) 423-2755	0.25	0.20
Duane Johnson	AMES	ddj@ameslab.gov	(515) 294-9649	–	–
Krishna Rajan	ISU	krajan@iastate.edu	(515) 294-2670	–	–

Project 2.3.2 is relying on the following activities:

1) State-of-the-art *ab initio* full-potential electronic structure calculations of solute effects on stability and magnetic properties led by **Per Söderlind**;
2) Alloying effect on stability and magnetic properties within *ab initio* Green function-based electronic structure methodology (to study for example the substitution of a REE or a transition metal element by another one on properties) led by **Alexander Landa**;
3) Effect of interstitial element and structural relaxation on properties by *ab initio* methodology (validated by full-potential based results), and development and maintenance of the search engine that build up the MDS, led by **Vincenzo Lordi**; and
4) Development and maintenance of the thermodynamic database for REE-based multi-component alloys, based on input data from experiments and *ab initio* energetics, led by **Patrice Turchi**.

Finally the project will benefit from the collaboration of **Duane Johnson** and **Krishna Rajan** on the impact of combinatorial discovery concepts and tools on MDS performance.

IV. Project Schedule and Deliverables for the Five-year Project

IV.1. Task 0: Project Kick-off

0. Initial meetings with CMI team members to review project plan and technical approach

• Refine research goals, complete literature search, identify and contact other project teams involved in experimental and other modeling activities that relate to this project (Q1-Q2).

IV.2. Task 1: Method Development and Validation of Materials Design Simulator

IV.2.A. Literature search for *ab initio* and thermodynamic studies of relevant magnetic REE-based alloys and compounds

• Complete literature search on REE alloy thermodynamic properties (Q1-Q2).

• Evaluate current state-of-the-art *ab initio* data for REE alloy thermodynamics. The critical parameters are: Gibbs energies, phases, magnetic moments, melting temperatures, and transformation temperatures (Q1-Q2).

Comments: In terms of targeted accuracy, our modeling effort will provide energies within 1 mRy/atom (i.e., 1.3 kJ/mole), temperature within 100-150 K, and magnetic moments within 1 Bohr magneton/atom.

IV.2.B. Implementation and validation of CALPHAD-based search engine

• Add magnetism to search constraints in search engine (Q1-Q3).

• Validate search for optimal magnetism for a known ternary REE alloy by comparing to experimental data with a target accuracy of 80% (Q6).

Comments: In the search engine, besides probing for stability, phase occurrence, and melting temperature, magnetic properties have also to be considered, and accuracy of better than 80% is expected, compared to available experimental data.

IV.2.C. Implementation and validation of spin-orbit coupling of f-electrons in *ab initio* electronic structure code

• Implement and test *f*-electron spin-orbit coupling (SOC) by calculating magnetic moments and ground-state properties as functions of composition for Fe-Co (Q3).

• Validate SOC for known Fe-Co system by comparing magnetic properties with experimental data with a target accuracy better than 80% (Q4).

• Compute and validate SOC for more complex REE alloy Sm-Co by comparing magnetism and ground-state properties to experimental data with a target accuracy of better than 80% (Q6).

Comments: Fe-Co has been selected since the plan is to consider the influence of Co and Fe on electronic structure, ground-state properties and magnetism when Fe and Co are mixed with a REE: accuracy of better than 80% is expected when compared to available experimental data

IV.3. Task 2: Application of the Materials Design Simulator to REE-based Alloys

IV.3.A. *Ab initio* electronic structure studies

• Q7-Q9-Q11-Q13-Q15-Q17 (one deliverable Qi every two quarters): *Ab initio* electronic structure, ground-state properties, and magnetism for **six** REE-based binary alloys relevant to CMI with comparison to experimental data when available, with a target accuracy of 80%.
Comments: Tasks 2A-C performed as part of feedback loop in MDS development and are not entirely independent.

IV.3.B. Development of a thermodynamic database for material search engine based on ab initio and experimental data

• Q8: Initial construction of thermodynamic database.
• Q10: Refinement of thermodynamic database for REE-containing alloys from existing experimental and other ab initio data.
• Q8-Q10-Q12-Q14-Q16-Q18 (one deliverable Qi every two quarters, in concert with the deliverables of Task 2.A)**:** Expand database to include additional REE-based alloys by using information from Task 2.A and available experimental data from other projects and scientific literature. The data will include for each phase the thermodynamic information (Gibbs energy of formation and transformation), melting temperatures, and magnetic properties. The target accuracy for these data will be 80%.
• Q19: Complete database of REE-based alloys relevant for CMI
Comments: Task 2B – The thermodynamic database and the thermo-physical data that are CMI relevant will be refined after feedback from experiments. After second year, enough results will be accumulated to study combination of binaries and solute effect on properties. These results will comprise Gibbs energies, stable phases, magnetic moments, melting temperatures, transformation temperatures, among others, that will be measured by others CMI projects

IV.3.C. Search for optimal REE-based magnet alloy compositions

• Q9: Prediction of a "known" reduced-REE-content magnet alloy. Strong interaction with other experimental projects is expected
• Q11: Prediction of one novel reduced-REE-content magnet alloy.
• Q13-Q15-Q17-Q15-Q19-Q20 (one deliverable Qi every two quarters, except for the last one, Q20, that will provide a summary for this task)**:** Prediction of additional novel reduced-REE-content magnet alloys and iteration with experimental fabrication/characterization.
Comments: In Task 2.C, the project will provide a user-friendly MDS tool to guide experiments in designing new magnet alloys with less RE content and improved performance

V. Accomplishments from September 2013 to March 2014

V.1. Activities for September 2013

1) • Turchi and Söderlind attended the CMI kick off meeting at Ames Lab (09/09-11/13), and participated in the discussions with members of other related projects to confirm the scope of the present project.
2) • The development of the thermodynamic database for REE-based alloys has been initiated, and phase diagram information has been generated for Co-Sm, Fe-Gd, and Co-Fe (Patrice Turchi).
3) • Electronic structure calculations for the entire series of 4f rare earth elements are performed. These include atomic volumes, bulk moduli, and magnetic moments. (Per Söderlind).

4) • Electronic structure and magnetic properties of Sm-based alloys has been initiated for the purpose of validating the thermodynamic database (Alexander Landa and Vincenzo Lordi).
5) • Additional papers on electronic structure and thermodynamic properties have been added to the reference list that is built for the project and CMI (Team).

V.2. Activities for October 2013

1) • The development of the thermodynamic database for REE-based alloys has been extended (Patrice Turchi).
2) • Electronic structure calculations for the entire series of 4f rare earth elements continue and ideas of writing an article is taking form (Per Söderlind).
3) • Electronic structure and magnetic properties of Sm-based alloys have been continued for the purpose of validating the thermodynamic database (Alexander Landa).
4) • Structural analysis of complex RE-based compounds has been initiated (Vincenzo Lordi).
5) • Additional papers on electronic structure and thermodynamic properties have been added to the reference list that is built for the project and CMI (Team).

V.3. Activities for November 2013

1) • The development of the thermodynamic database for REE-based alloys has been extended, and now includes the thermodynamic properties of seven binaries alloys (Patrice Turchi)
2) • Electronic structure calculations for the entire series of 4f rare earth elements are close to completed but needs to be analyzed (Per Söderlind).
3) • Electronic structure and magnetic properties of Sm-based alloys have been extended for the purpose of validating the thermodynamic database (Alexander Landa and Vincenzo Lordi).
4) • Work on structural analysis of complex RE-based compounds has been extended in November (Vincenzo Lordi).
5) • Additional papers on electronic structure and thermodynamic properties have been added to the reference list that is built for the project and CMI (Team).

V.4. Activities for December 2013

1) For the study of the thermodynamic properties of the quaternary Co-Fe-Gd-Sm system, all the six binaries have been evaluated; and for the ternary B-Co-Fe system, the three binary subsystems have been evaluated. In the months to come, the introduction of Pr and Nd in the quaternary Co-Fe-Gd-Sm system will necessitate the evaluation of the properties for the additional eight binary subsystems, and the introduction of Nd in the ternary B-Co-Fe will require the evaluation of the thermodynamic properties of three additional binary subsystems. This work will allow us to start testing our search engine, *i.e.*, our materials design simulator. (Patrice Turchi).
2) The results from DFT calculations within various approximations for all the REE (except the two divalent ones) were obtained to confirm whether or not the trends in fundamental properties such as atomic volumes and magnetic moments are realistically reproduced. A state-of-the-art all-electron, full-potential treatments assuming the fcc crystal structure and an ferromagnetic order was applied. The various approximations that were considered are: (1) Electron exchange and correlation: LDA (local density approximation) and GGA (generalized gradient approximation); (2) Semi-relativistic (SR; all relativistic effects except spin-orbit coupling, SOC); (3) SR+SOC; (4) SR+SOC+orbital polarization (SR+SOC+OP). The results need now to be analyzed, and we anticipate soon a publication summarizing all these results. (Per Söderlind).
3) Electronic structure and magnetic properties of the Co-Fe-Sm system were conducted and the results will be analyzed in the months to come (Alexander Landa).
4) Electronic structure calculations for ordered Co-Fe-Sm structure were initiated to validate data from the thermodynamic database and better understand the alloying role on magnetic properties (Vincenzo Lordi).
5) All four of us added references to our CMI bibliography (64 pages) that primarily focuses on thermodynamic and magnetic properties (Team).

V.5. Activities for January 2014

1) For the study on the thermodynamic properties of the quaternary Co-Fe-Gd-Sm system, all the six binaries have been evaluated; and for the ternary B-Co-Fe system, the three binary subsystems have been evaluated.

The thermodynamic information on the binary systems has been collected in one single file to treat multi-component alloy systems, and this task required to make the Gibbs energy models for all phases fully compatible. This task should be completed next month (Patrice Turchi).

2) All the results from DFT calculations within various approximations for all the REE (except the two divalent ones) have been collected and analyzed, and a publication summarizing all these results on equilibrium volume, bulk modulus, and magnetic moment, will be submitted in the near future to Phys. Rev. B. (Per Söderlind).
3) Electronic structure and magnetic properties of the Co-Fe-Sm system were conducted and the results are still being analyzed (Alexander Landa).
4) Electronic structure calculations for ordered Co_5Sm structure were completed to validate data from the thermodynamic database and better understand the alloying role on magnetic properties (Vincenzo Lordi).
5) All four of us added references to our CMI bibliography (71 pages) that primarily focuses on thermodynamic and magnetic properties (The team).
6) The second quarterly report has been submitted to Ames Lab during the month of January.

V.6. Activities for February 2014

1) For the study on the thermodynamic properties of the quaternary Co-Fe-Gd-Sm system, all the six binaries have been evaluated; and for the ternary B-Co-Fe system, the three binary subsystems have been evaluated. The thermodynamic information on the binary subsystems that make up Co-Fe-Gd-Sm and B-Co-Fe is has been collected in one single file to treat multi-component alloy systems, and this task required to make the Gibbs energy models for all phases fully compatible. This task has been delayed a bit and will be completed next month since Patrice Turchi has been on sick leave for two weeks.
2) All the results from DFT calculations within various approximations, including SR, SR+SO, SR+SO+OP, for all the REE (except the two divalent ones) and also GGA+U and hybrid functional for Sm, have been collected and analyzed, and a publication has been submitted to Phys. Rev. B. (Per Söderlind, Alexander Landa, Vincenzo Lordi and Patrice Turchi).
3) Electronic structure and magnetic properties of the Co-Fe-Sm system were computed and the results are still being analyzed (Alexander Landa).
4) Electronic structure calculations for ordered Co_5Sm structure were completed to validate data from the thermodynamic database and better understand the alloying role on magnetic properties (Vincenzo Lordi).
5) The plan for future work has been revisited and it was decided that the focus will be on the electronic and thermodynamic properties of $(Sm,Gd,Dy)_2(Co,Fe)_{17}$.

V.7. Activities for March 2014

1) The thermodynamics of the quaternary Co-Fe-Gd-Sm system has been assembled in one database by making the Gibbs model description compatible for similar phases occurring in the binary subsystems (Patrice Turchi).
2) Electronic structure results for Co5Sm have been benchmarked by comparison with the results from other electronic structure calculations (Vincenzo Lordi, Alexander Landa, and Per Söderlind).
3) Electronic structure calculations for fcc-based Sm-Co system have been completed, and the results for the electronic structure and magnetic properties of Co-Fe-Sm are still analyzed (Alexander Landa).
4) Crystal structure of the Sm_2Co_{17} phase of Sm-Co alloy has been analyzed and input file for its description has been created for studies with various Density Functional theory (DFT)-based methods (Vincenzo Lordi, Alexander Lordi, and Per Söderlind).
5) CMI report on 2.3.2 project has been completed (Patrice Turchi, Per Söderlind, Alexander Landa, and Vincenzo Lordi). 16 pages.

In the following subsections V.8-A to E, we present a summary of the results that have been obtained from July 2013 to March 2014.

V.8.A. Ground-state properties of RE metals: An evaluation of density-functional theory (Per Söderlind, P. E. A. Turchi, A. Landa, and V. Lordi)

This subsection presents the abstract and a summary of the results extracted from a manuscript entitled "Ground-state properties of rare–earth metals: An evaluation of density functional theory", authored by P. Söderlind, P. E. A. Turchi, A. Landa, and V. Lordi, which has been submitted in February 2014 to Phys. Rev. B for publication (LLNL-JRNL-649338).

Abstract: The RE metals have important technological applications due to their magnetic properties but are scarce and expensive. Development of high-performance magnetic materials with less rare-earth content is pursued but theoretical modeling is hampered by complexities of the rare earths electronic structure. The existence of correlated (atomic-like) 4f electrons in the vicinity of the valence band makes any first-principles theory exceedingly difficult. Nevertheless, we apply and evaluate the efficacy of density-functional theory for the series of lanthanides (rare earths) investigating the influence of the electron exchange and correlation functional, spin-orbit interaction, and orbital polarization. The results are compared with those of the so-called "standard" model of the lanthanides in which electrons are constrained to 4f core states with no hybridization with the valence electrons. Our results suggest that spin-orbit coupling and orbital polarization are important, particularly for the magnetic properties, and that calculated equilibrium volumes, bulk moduli, and magnetic moments show correct trends overall. However, the precision of the calculated properties is not at the level of that found for simpler metals in the Periodic Table, and the electronic structures do not accurately reproduce x-ray photoemission spectra.
This thorough quantum-mechanical based study on the REE has been initiated early on to establish the efficacy of the general approach (density-functional theory) and to provide a necessary reference for subsequent work on alloys and compounds. The goal is to test the impact of various possible approximations that could be considered is state-of-the-art *ab initio* Full-Potential Linear Muffin-Tin Orbital (FP-LMTO) calculations on ground state (atomic volume, bulk modulus) and magnetic properties along the 4f series (except for the 2 divalent elements Eu and Yb of the periodic table. The various approximations that were considered are: (1) Electron exchange and correlation: LDA (local density approximation) and GGA (generalized gradient approximation); (2) Semi-relativistic (SR; all relativistic effects except spin-orbit coupling, SOC); (3) SR+SOC; (4) SR+SOC+orbital polarization (SR+SOC+OP). The results are displayed in Figs. 2-5.

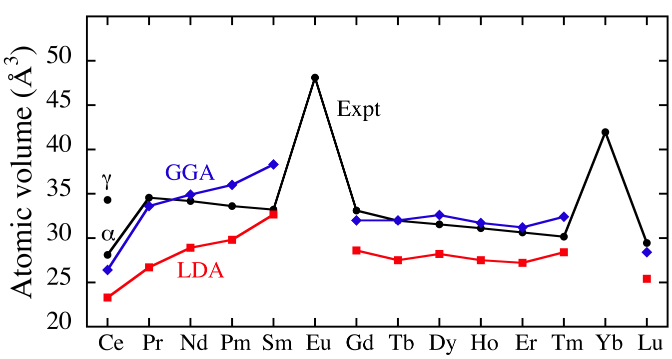


Fig. 2. Experimental room-temperature atomic volumes with LDA+OP and GGA+OP results (4*f*-band model). The experimental volume for both α-Ce and γ-Ce is shown.

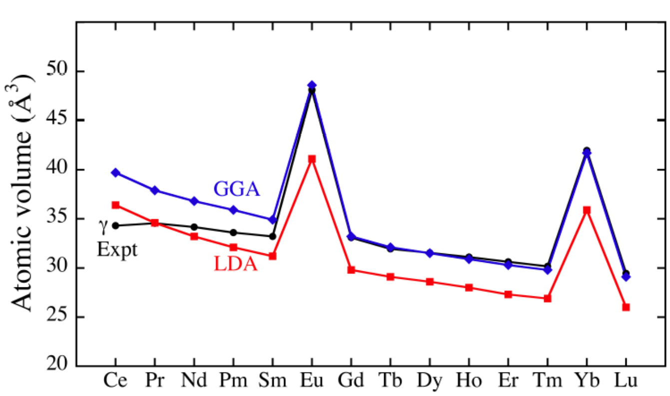


Fig. 3. Experimental room-temperature atomic volumes with LDA and GGA results (4*f*-band model). The experimental volume for γ-Ce is shown.

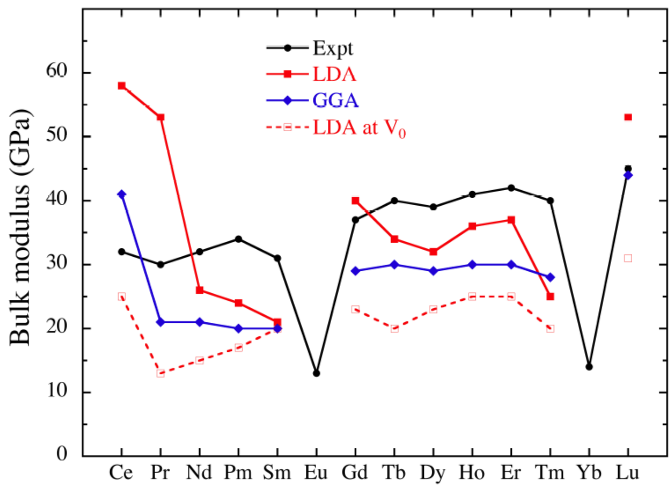


Fig. 4. Experimental average bulk modulus together with LDA+OP and GGA+OP (4*f* band model) results. Open symbols refer to LDA+OP calculations of B evaluated at the experimental atomic volume (V0). For Ce, the experimental result for the α phase (at 1 GPa) is shown.

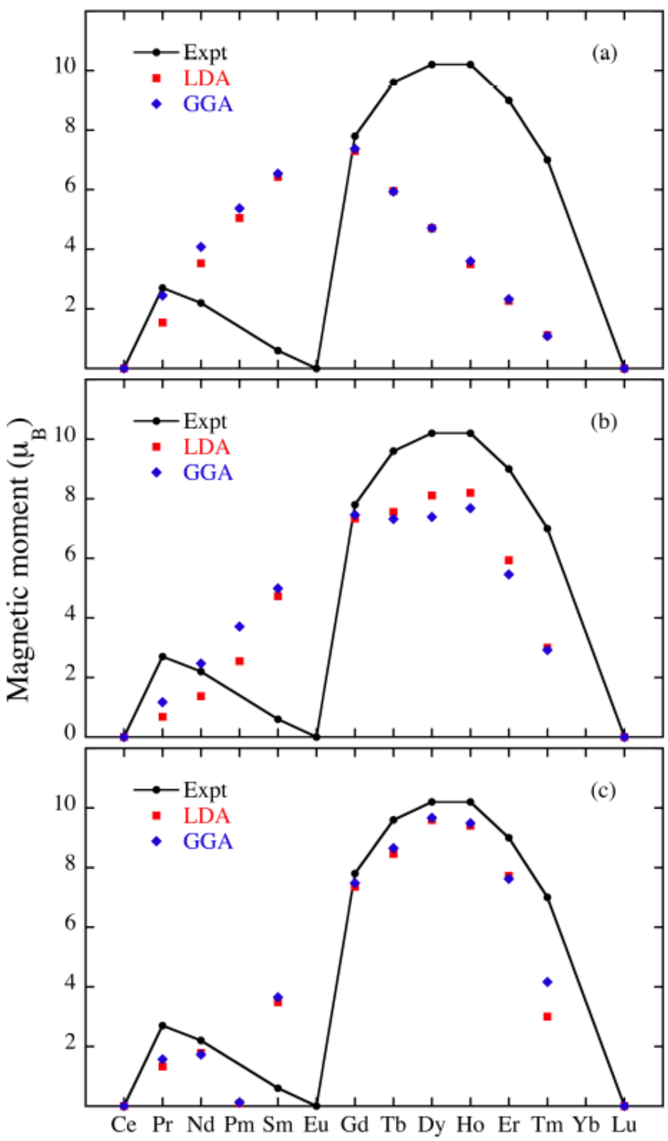


Fig. 5. Experimental total magnetic moments together with results from the 4*f*-band model (LDA and GGA) with SP (a), SOC (b), and OP (c) interactions.

Despite the limitations clearly revealed in this study, parameter-free electronic structure calculations founded on DFT can be useful for identifying trends in solute effects on stability and magnetic properties in RE-based multi-component alloys, and this knowledge can provide useful guidance for selecting specific solutes that minimize the usage of RE metals without altering materials performance. This conclusion allows us to then extend this work with confidence (and awareness about some of the limitations) to alloys and compounds, and make use of the results on energetics to assess the thermodynamic of complex REE-based systems. This project will also benefit of other activity geared toward improving the electronic structure description for this class of elements.

V.8.B. DFT benchmark of REE (Sm testing) (V. Lordi, A. Landa, and P. Söderlind)
In addition to the systematic DFT study of the REE metals (in fcc structure), additional detailed benchmark studies were performed on Sm, which is the most difficult non-divalent REE to describe. In particular, application of GGA with spin-orbit and orbital polarization still fails to predict the large orbital magnetic moment of Sm by 2–3 times, and also slightly overestimates the atomic volume. To investigate this further, a series of studies were performed using GGA+U and hybrid X-C functional to investigate correlation effects as well as a comparison between fcc and hcp structures. We find that atomic volume, bulk modulus, spin and orbital magnetic moments are very similar between the hcp and fcc structure, due to the identical local structures (only stacking sequence differs). The GGA+U method is often used as a computationally inexpensive way to treat some kind of electron correlation, particularly to localize (or delocalize) *d* or *f* electrons, which standard DFT may fail to describe properly. We performed GGA+U calculations on fcc Sm, varying $U_{eff} = U - J$ from 2 to 7 eV to cover the range of reasonable values for U_{eff} on the 4*f* electrons. The general result is that atomic volume increases and bulk modulus decreases with increasing U_{eff}, producing a worse agreement with experiment compared to $U_{eff} = 0$. In addition, the magnitude of the orbital moment also decreases slightly, so no improvement in the magnetic properties is obtained by applying the +U. Another approach to increase localization from electron correlation in a more *ab initio* sense is to apply a hybrid functional, which mixes some Hartree-Fock exact exchange with a traditional DFT x-c functional. We applied the popular screened hybrid HSE06 to hcp Sm as another test. Despite the enormous computational expense, the result was an even worse description of the orbital moment than either GGA or GGA+U, with the prediction about 20 times smaller than experiment.

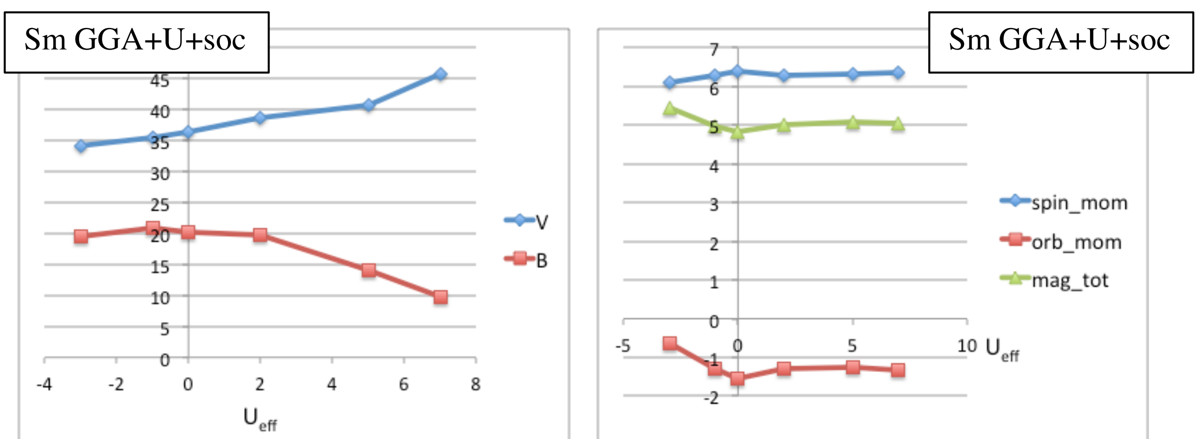
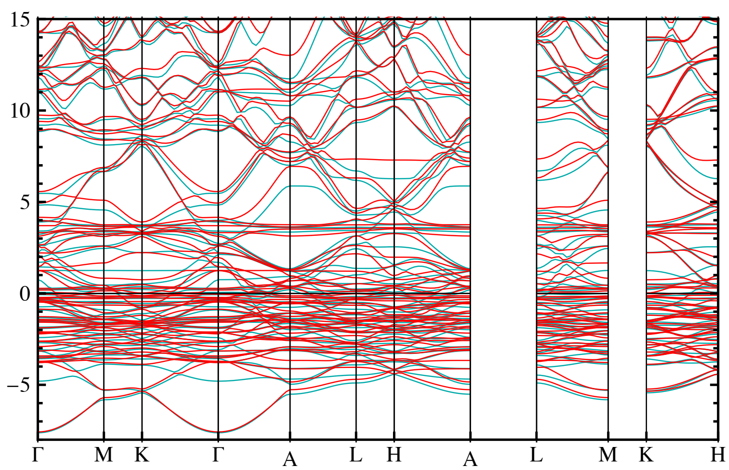


Fig. 6. (Left) Calculated atomic volume and bulk modulus; and (Right) magnetic properties (spin moment, orbital moment, and total magnetic moment), as functions of U_{eff} for fcc-based Sm within GGA+U+SOC level of approximation.

Co_5Sm benchmark: The Co_5Sm system serves as an appropriate benchmark system for a dilute REE magnet material, since it contains only 16% REE and includes Sm, which is the most difficult REE metal for DFT to properly describe the magnetic properties. However, since Sm is a minority element in the compound, GGA describes the physical and magnetic properties quite well, which is a good DFT validation result. We calculated the equilibrium unit cell volume, bulk modulus, spin density of states, band structure, and non-collinear magnetic moments to compare to experiment. The results based on calculations performed with the Vienna *Ab Initio* Simulation Package (VASP) are summarized in the Table I below. Unlike in the REE pure metals, spin-orbit coupling does not significantly affect the results for Co_5Sm. However, since Co_5Sm is ferrimagnetic, non-collinear magnetic calculations are required to properly describe the local magnetic and orbital moments in the material, and also the spin density of states depends on the spin-orbit interaction. The result is a total magnetic moment aligned with the crystal's *c*-axis of 3.7 μ_B/unit cell (1.7 μ_B/unit cell spin moment + 2.0 μ_B/unit cell orbital moment). SR-EMTO and FP-LMTO (GGA+OP) methods were also applied to Co_5Sm, with similar results (see Table I). We notice that the results are fairly similar but the all-electron methods give larger spin moments (2.09 and 2.1 μ_B/unit cell), and in the case of the FP-LMTO, a much larger orbital moment as well (4.0 μ_B/unit cell) caused by the orbital polarization effect accounting in the FP-LMTO code.

	VASP	VASP+SOC	SR-EMTO	FP-LMTO	Expt.
Unit cell volume (Å^3)	84.20	84.25	86.65	84.41	85.61
Bulk modulus (GPa)	134.5	134.1	124	123	
Bulk modulus derivative	4.71	4.72	4.06	3.00	
Spin moment (μ_B/unit cell)	1.70	1.71	2.09	2.1	
Orbital moment (μ_B/unit cell)	n/a	2.01	n/a	4.0	
Total moment (μ_B/unit cell)	1.70	3.72	2.09	6.1	

Table I. Equilibrium unit cell volume, bulk modulus and its derivative, and magnetic properties (spin, orbital, and total moment) of Co_5Sm as functions of the *ab initio* methodology (see text).



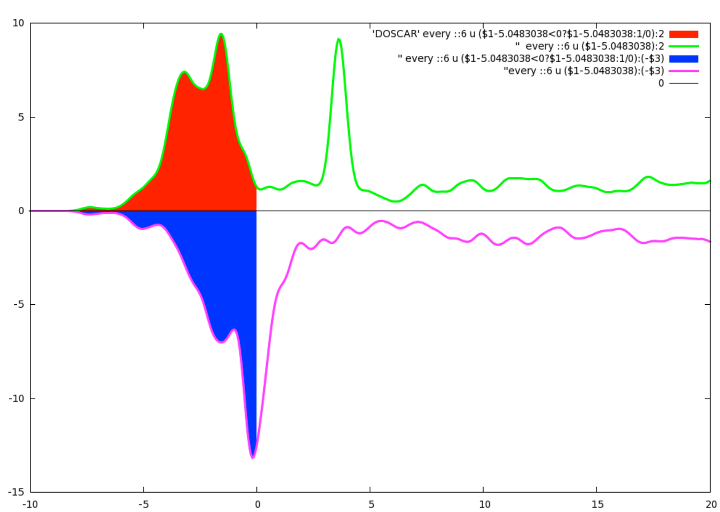


Fig. 7. Spin-resolved band structure (Top) and density of states (bottom) of Co_5Sm within PBE+SOC (see text).

V.8.C. DFT calculations for fcc-based Sm-Co alloys (A. Landa)
In addition to spin-polarized SR-EMTO calculations for $SmCo_5$ compound, already reported by Vince Lordi, spin-polarized Green's function based Korringa-Kohn-Rostoker-Atomic Sphere Approximation-Coherent Potential Approximation (KKR-ASA-CPA) calculations have been performed with the Coulomb screening potential end energy for Sm-Co disordered fcc alloys. The screening constants, α and β, are determined from the supercell calculations using locally self-consistent Green's function (LSGF) method. For the Sm-Co alloys the α and β screening constants are found to be 0.649 and 1.025, respectively, and the charge transfer form Sm to Co atoms for the equi-atomic $Sm_{50}Co_{50}$ alloys was found to be significantly large (~ 0.561). Calculated heat of formation, atomic volume, and the bulk modulus for ferrimagnetic fcc Sm-Co alloys are shown in Fig. 8.

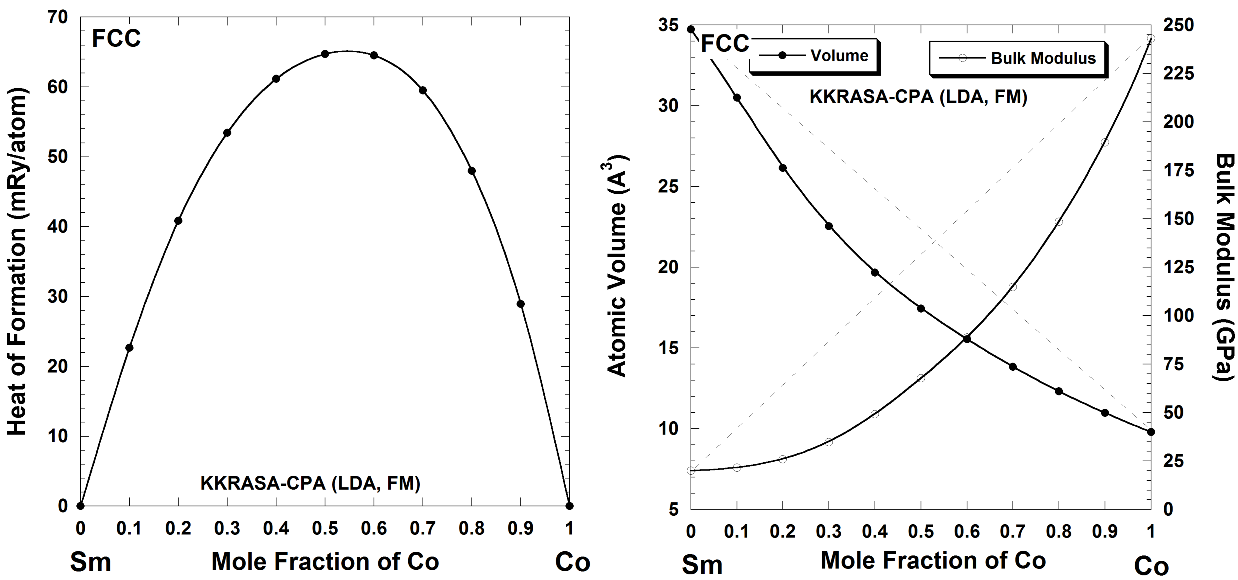


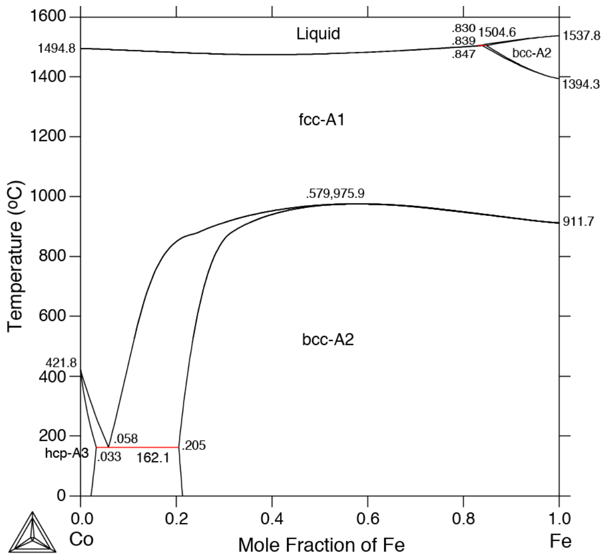
Fig. 8. Heat of formation, atomic volume, and bulk modulus of fcc Sm-Co alloys versus alloy composition calculated within the spin-polarized KKR-ASA-CPA Green's function electronic structure method.

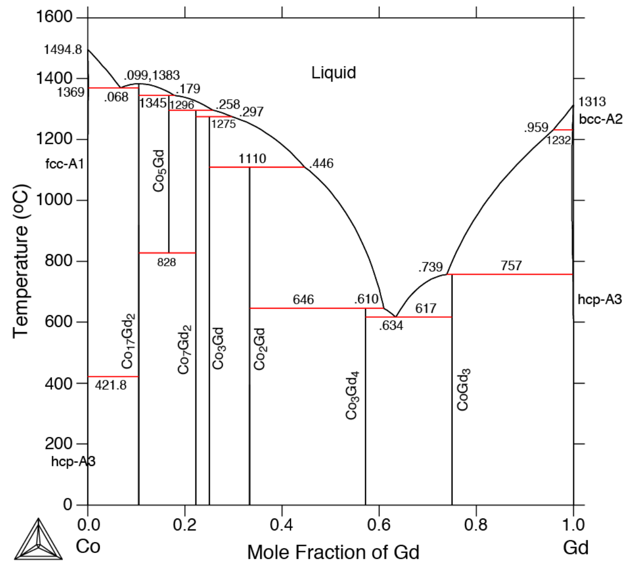
These calculations show a significant positive heat of formation for fcc Sm-Co solid solutions (no such solutions are found in the experimental Sm-Co phase diagram), which is asymmetrical and shifted around the equi-atomic composition towards the smaller component (Co), the negative deviations from Zen's law (magnetism is involved) and significant softening of the bulk modulus within the whole compositional range, as shown in Fig. 8.

V.8.D. Thermodynamics of REE-based alloys (P. E. A. Turchi, A. Landa, P. Söderlind, and V. Lordi)
Based on the CALPHAD methodology, the thermodynamics of the following systems has been assessed:

1) Co-Fe-Gd-Sm: Co-Fe, Co-Gd, Co-Sm, Fe-Gd, Fe-Sm, Gd-Sm
2) Co-Fe-Nd: Co-Fe, Co-Nd, Fe-Nd
3) B-Co-Fe: B-Co, B-Fe, Co-Fe

The thermodynamic database that has been assembled to describe the binary alloy systems leads to phase diagrams that are compatible with the known experimental assessments. A sample of the phase diagrams (based on their full thermodynamic description) obtained so far is shown in Fig. 9.


Liquid
fcc-A1
bcc-A2
hcp-A3
1494.8
1537.8
1394.3
1504.6
.830
.839
.847
.579,975.9
911.7
421.8
.058
.033
162.1
.205
Temperature (oC)
Mole Fraction of Fe
Co
Fe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hcp-A3
bcc-A2
hcp-A3
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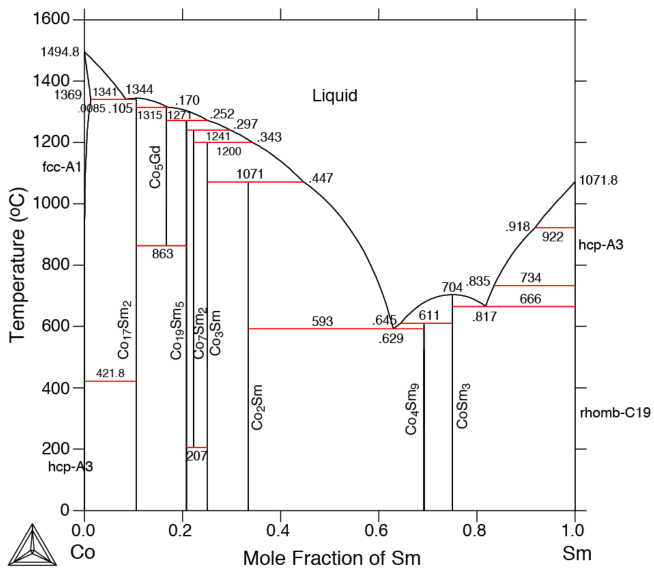
.099,1383
1345
.179
1296
1275
.258
.297
1110
.446
828
421.8
646
.610
.634
617
.739
757
.959
1232
1313
$Co_{17}Gd_2$
Co_5Gd
Co_7Gd_2
Co_3Gd
Co_2Gd
Co_3Gd_4
$CoGd_3$
Temperature (oC)
Mole Fraction of Gd
Co
Gd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hcp-A3
hcp-A3
rhomb-C19
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1369
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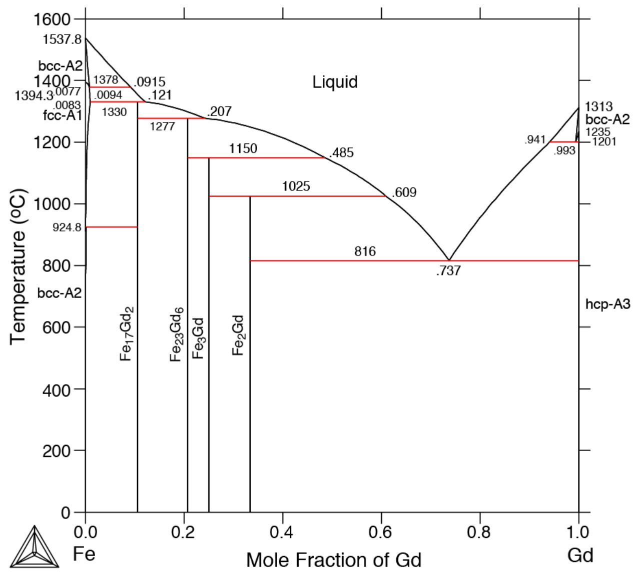
.105
1341
1344
1315
1271
.170
.252
.297
1241
1200
.343
1071
.447
863
421.8
207
593
.645
.629
611
704
.835
.817
734
666
.918
922
1071.8
$Co_{17}Sm_2$
Co_5Gd
$Co_{19}Sm_5$
Co_7Sm_2
Co_3Sm
Co_2Sm
Co_4Sm_9
$CoSm_3$
Temperature (oC)
Mole Fraction of Sm
Co
Sm


Liquid
bcc-A2
fcc-A1
bcc-A2
hcp-A3
bcc-A2
1537.8
1394.3
.0077
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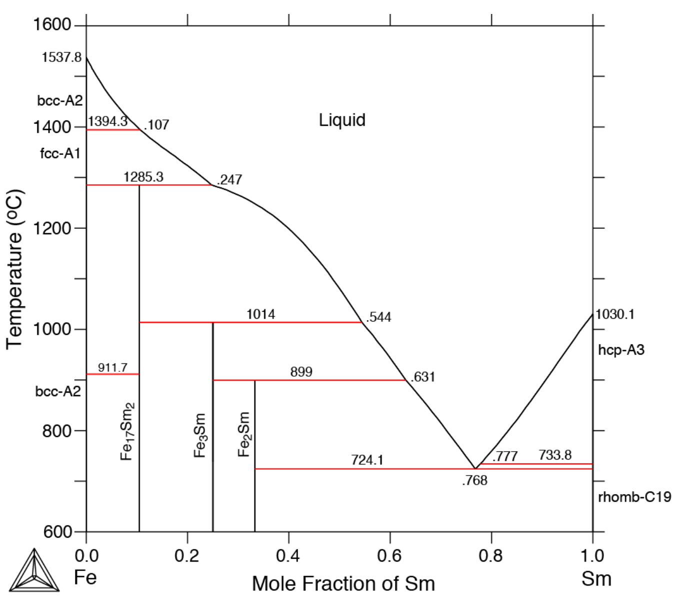
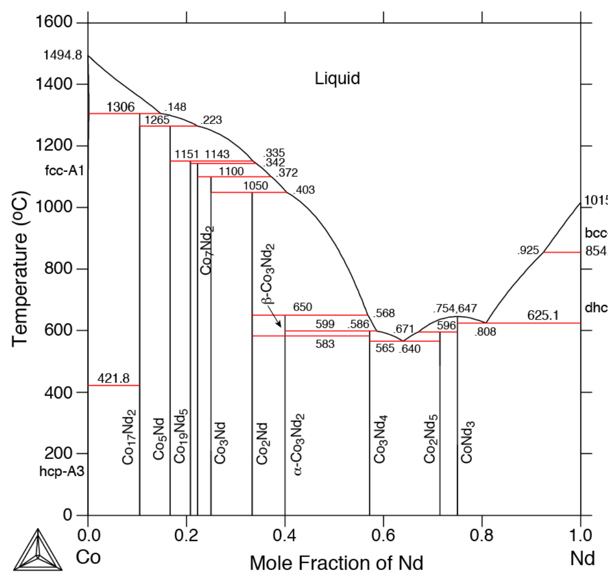
.0094
.0915
.121
1330
1277
.207
1150
.485
1025
.609
924.8
816
.737
.941
.993
1235
1201
1313
$Fe_{17}Gd_2$
$Fe_{23}Gd_6$
Fe_3Gd
Fe_2Gd
Temperature (oC)
Mole Fraction of Gd
Fe
Gd


Liquid
bcc-A2
fcc-A1
bcc-A2
hcp-A3
rhomb-C19
1537.8
1394.3
.107
1285.3
.247
1014
.544
911.7
899
.631
724.1
.768
.777
733.8
1030.1
$Fe_{17}Sm_2$
Fe_3Sm
Fe_2Sm
Temperature (oC)
Mole Fraction of Sm
Fe
Sm


Liquid
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hcp-A3
bcc-A2
dhcp
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1306
148
1265
.223
1151
1143
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.342
.372
1100
1050
.403
421.8
650
599
.586
583
.568
565
.640
.671
.754,647
596
.808
625.1
.925
854.7
1015.8
$Co_{17}Nd_2$
Co_5Nd
$Co_{19}Nd_5$
Co_7Nd_2
Co_3Nd
β-Co_3Nd_2
Co_2Nd
α-Co_3Nd_2
Co_3Nd_4
Co_2Nd_5
$CoNd_3$
Temperature (oC)
Mole Fraction of Nd
Co
Nd

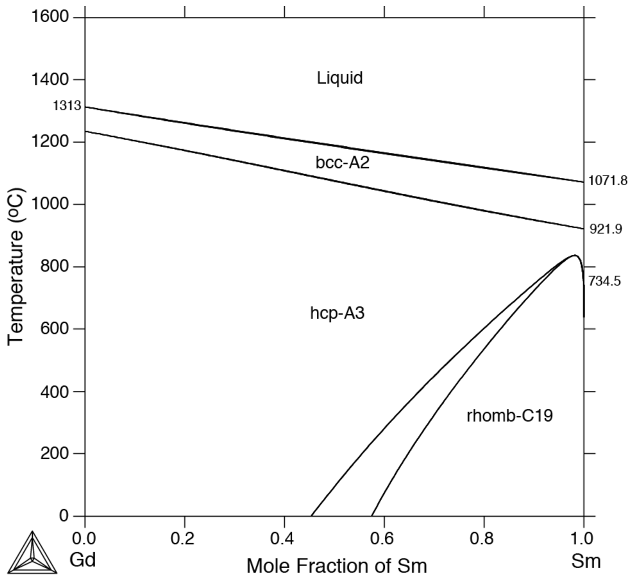

Fig. 9. Thermodynamic assessment (from top to bottom, and left to right) of Fe-Co, Co-Gd, Co-Sm, Fe-Gd, Fe-Sm, Co-Nd, and Gd-Sm alloy systems within the CALPHAD methodology.

V.8.E. CMI Bibliography (P. E. A. Turchi, A. Landa, P. Söderlind, and V. Lordi)
Since the beginning of the project, we are assembling a bibliography, that is constantly updated (73 pages as of March 24th 2014), focusing on the thermodynamic, magnetic, and electronic structure properties of REE-based alloys and compounds (P.S.: no references to oxide, or materials in aqueous medium). We would like to suggest to have a capability to store this valuable information on a secure website site so that CMI members can take advantage of it, and add their own references.

VI. Plan for the Near Future (until the end of year 2)

VI.1. Electronic Structure Studies

It has been decided that CMI would greatly benefit from an in-depth study of the complex alloys based on the RE_2TM_{17} structure, see Fig. 10, where RE (Rare Earth)=Sm, Gd, Dy, and TM (Transition Metal)=Fe, Co-Ni to better understand the role of RE and TM substitutions and of interstitials such B or N on magnetic properties. This will be done with the most accurate Full-Potential Linear Muffin-Tin Orbital (FP-LMTO) code for the compounds, the Exact Muffin-Tin Orbital-Coherent Potential Approximation (EMTO-CPA) for the treatment of chemical disorder (substitutional defects), and with the Vienna *Ab Initio* Simulation Package (VASP) code for the treatment of interstitials for which case atomic relaxations must be considered. Because the studies on RE_2TM_{17} compounds require highly computer-intensive calculations and hence the use of high-performance computers, the preliminary benchmarking study that has been performed so far has been based on the VASP code. The VASP code, however, does not possess the robustness and accuracy of the FP-LMTO for *f*-electron systems and has no implementation of orbital polarization (important for magnetic moments). Therefore, unless computationally impossible, FP-LMTO is the preferred tool for the most accurate treatment of the REE-based alloy systems. Also, EMTO calculations are currently performed for Sm_2Co_{17} and Sm_2Fe_{17} (Th_2Zn_{17}-type) compounds with the ultimate plan to calculate $Sm_2(Fe_xCo_{1-x})_{17}$ solid solutions.

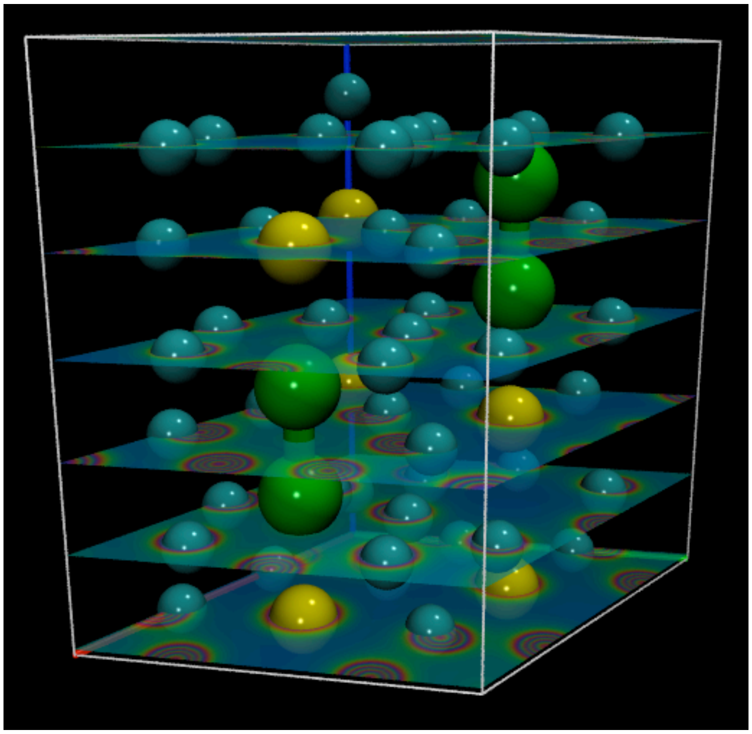

Fig. 10. Crystal structure of the Sm_2Co_{17} phase of Sm-Co alloy. The yellow and green atoms represent Sm whereas the smaller blue atoms represent Co.

The very first compound that has been selected, namely Sm_2Co_{17}, will serve as the basis for subsequent studies on solute effect on properties of RE_2TM_{17} (and doped compounds). The $(Sm,Gd,Dy)_2(Co,Fe)_{17}$ system has been identified as a target material for study in the short-to-medium term. Based on our benchmarking work on the REE metals and Co_5Sm using high-level DFT approximations, we are confident that the same level of DFT theory will adequately describe the magnetic properties of this dilute REE compound. We are currently computing the ground state structural and magnetic properties of the base compound Sm_2Co_{17} in the rhombohedral structure (57 atoms in the unit cell). This base compound will serve as a test bed for future work in introducing different impurities either substitutionally or interstitially (Gd, Dy, Fe, Co) in different concentrations to study the modifications of the magnetic properties and determine the correlations with the structural modifications (changes in crystal symmetry,

VI.2. Thermodynamic Properties

The next steps in the development of a thermodynamic database for REE-based alloys for the near future are:

- Study of the ternary Co-Fe-Nd
- Study of the ternary B-Co-Fe
- Study of the quaternary (Gd,Sm)(Co-Fe)
- Introduction of Nd in B-Co-Fe
- Introduction of Pr and Nd in the quaternary system Co-Fe-Gd-Sm

VI.3. Initial Development and Applications of the MDS

Once a sufficient number of systems will be thermodynamically assessed, and possibly validated by experiments, the MDS (after an upgrade that will allow for a search for optimum magnetic properties, besides, phases, melting temperature, and range of stability) will make use of this thermodynamic database (that also includes information on the magnetic properties) to search for the most promising combination of elements and their composition range for hard magnet applications.

VII. Conclusions

Despite decrease in funding in November that slowed down our productivity, the results obtained so far are those we originally promised to deliver within a month or so. Besides the electronic structure studies and thermodynamic assessments that will continue, we will focus on assembling the thermodynamic data to exercise the Materials Design Simulator – MDS – (after update of the search engine software component) for multi-component REE-based alloys and compounds to demonstrate as soon as possible the potential application of this tool within CMI, so theory and modeling are not out of sync with experiments (which is always a possibility).

1) **Why this project should be funded at all?** To make scientifically-based decision on a proper selection of potential substitutes for REEs, one has to build materials knowledge by putting together a validated thermodynamic database, and exercising a thermodynamic software coupled to an efficient search engine to figure out which phase should form with specific properties as functions of temperature, composition, pressure, possibly system size (bulk or nano-materials) and most importantly solute element.

2) **Are sure can you be that you will get results out of this approach?** At LLNL we have been working on this approach for several years, and we successfully applied it to 5f elements (actinides) and their alloys with programmatic applications and also applications to nuclear materials science. This approach has also been successfully applied to some extent in academia to structural materials.

3) **Why should experimentalists bother about this proposed MDS?** Making available a user-friendly MDS (materials design simulator) that can predict materials properties would help accelerate the development of new materials that make use of substitutes to REEs within a sound scientific way, and the synergy gained by coupling modeling to experiments would augment our overall knowledge of REE-based materials. The MDS would also guarantee the accelerated and safe insertion of materials into applications.

4) **Can this project be a stand-alone activity**? Yes and no. Yes in the early stage: the gathering of data from current literature and the development of a thermodynamic database with what is already known and available will be the core of the first year activity. Quantum-based calculations will also be carried out to supplement the database with some critical data (heats of formation, magnetic moments, *etc*.). However very soon after the first year, input from experimental data generated by the CMI team will be an important source of information to use not only to exercise the MDS, but also to validate and uniquely certify the accuracy of the simulator, and guarantee a safe and optimum insertion of new materials in engineering applications.

Acknowledgements

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DEAC52-07NA27344. This research is supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.